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A STUDY IN BONDING: METAL TO GLASS TO CERAMICS

**WILLIAM F. ZIMMERMAN
W. J. PLANKENHORN
DWIGHT G. BENNETT**

UNIVERSITY OF ILLINOIS

MARCH 1952

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A STUDY IN BONDING: METAL TO GLASS TO CERAMICS

*William F. Zimmerman
W. J. Plankenhorn
Dwight G. Bennett*

University of Illinois

March 1952

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**Wright Air Development Center
Air Research and Development Command
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FOREWORD

This report, No. 60, was prepared by W. F. Zimmerman, W. J. Plankenhorn and D. G. Bennett, at the University of Illinois in the Department of Ceramic Engineering. Presented herein are the results of experiments involving the bonding of high alumina and zircon porcelains, and of cordierite glasses. This work was accomplished for the U. S. Air Force under the provisions of Contract No. W33(038)ac-14520. The technical phases of the contract are administered by the Power Plant Laboratory of the Wright Air Development Center, with Mr. B. L. Paris acting as Project Engineer. It is identified as a project No. 1035 under E. O. No. R-506-67, Ceramics for Reciprocating Engines.

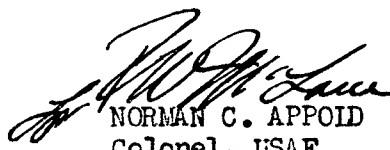
ABSTRACT

Ceramic tile pieces approximately 1 in. thick and either 1/4 in., 1/2 in., or 1 in. square were prepared from a high alumina porcelain, a zircon porcelain and a cordierite body. These ceramic specimens were fired in contact with the porcelain enameled surface of low carbon sheet steel approximately .052 in. thick. An enamel of low softening point (900°F.) and two series of graded expansion laminated coatings were used as the bonding medium in an effort to reduce shear stresses caused by the differential contraction of metal and ceramic. Smaller tile size, greater body porosity and retarded cooling rate seemed to aid in the development of a bond. Although it was possible to firmly attach the alumina, zircon and cordierite bodies to metal under favorable conditions, an extremely high stress level was generally indicated.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or the conclusions contained therein. It is published primarily for the exchange and stimulation of ideas.

FOR THE COMMANDING GENERAL:



NORMAN C. APPOLD
Colonel, USAF
Chief, Power Plant Laboratory
Aeronautics Division

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A STUDY IN BONDING: METAL TO GLASS TO CERAMICS

I. INTRODUCTION

Certain applications of ceramic materials involving their electrical or refractory characteristics require that they be attached in some manner to metals. This is generally accomplished by mechanical means, although a soldered joint is more often employed in the case of electronic components. For the fastening of insulating refractory materials to sheet metal structures operating at elevated temperatures, these methods might tend to become either unduly complicated, in the case of mechanical attachment, or expensive and time consuming, if soldered joints were used. On the other hand, if it were possible to utilize modified enameling practice to obtain a glass bond between steel and ceramic materials, it might then be both practical and inexpensive to apply refractory insulating materials over extensive areas of sheet metal exhaust components. Because of the high refractoriness and low thermal conductivity of ceramic materials these components might then operate at lower metal temperatures and extended life, or at higher operating temperatures and greater efficiencies. With these possibilities in mind, this investigation was directed toward the evaluation of modified enameling methods, enamel compositions and firing treatment in the formation of an enamel (glass) bond between steel and three ceramic materials - a high alumina porcelain, a zircon porcelain and a cordierite body.

II. DISCUSSION OF THE PROBLEM

1. Basic Considerations

The joining of a ceramic body to metal by means of a viscous glass is relatively simple at elevated temperatures; if the glass wets both the metal and the ceramic, the parts are joined. However, at temperatures at which this is possible the seal is somewhat fluid. The major problem is to prevent this glass seal from fracturing under thermal stresses when it is cooled to room temperature.

With regard to the relief of internal stresses within a glass, there are three stages in the cooling of a glass bonding medium. (1) As the glass starts to cool from the sealing temperature it is mobile enough to permit instantaneous stress relief by viscous flow. (2) With further cooling the viscosity increases to such a value that a finite time is required to release internal stresses. This is known as the annealing range. The viscosity of most glasses in the annealing range is

about 2.5×10^{13} poises. (3) Below this region the time required to relieve stress increases rapidly until a temperature is reached at which, for all practical purposes, the glass is infinitely viscous. From the above it follows that the rate of relief of internal stress is a function of time and of the viscosity of the glass (the viscosity of a glass composition is in turn dependent upon the temperature).

In joining materials of such dissimilar coefficients of thermal expansion as metal, glass and ceramics, stress is produced in the glass by the differential thermal contraction of the component parts. The magnitude of the stress is influenced by the modulus of elasticity of the glass. Only that thermal contraction which occurs below the temperature range of stress relief is effective in producing internal stresses. (See Figure 1)

Failure of the glass joint may occur as a result of the stresses described above. In attempting to bond ceramics to steel a fundamental consideration should be the formation of these stresses during cooling and the methods of reducing them below the point of failure. The following possibilities are listed for reducing the stress levels in glass bonds joining metal and ceramic components:

- a. Use of materials of matched coefficients of thermal expansion.
- b. Use of a glass having a low softening point.
- c. Absorption of stresses by yielding.
 - (1) within the metal
 - (2) within the glass (elastically)
 - (3) within the body
- d. Annealing of glass bonding zone.

a. Use of materials of matched coefficients of thermal expansion. The formation of a low stress bond between a glass and metal of nearly identical instantaneous thermal expansion rates forms the basis of a wide area of technology covering the so-called "matched" glass to metal seals. This same principle might apply to a metal-glass-ceramic joint in which both the glass and ceramic components possessed thermal expansion curves similar to that of steel. Magnesium oxide, for example, is one ceramic material which meets this requirement. However, in this study only lower expansion ceramic materials of better thermal shock resistance were investigated.

b. Use of a glass having a low softening point. Stresses due to differential thermal contraction may be decreased by reducing the magnitude of the contraction through the use of a glass bond of extremely low softening point.

Jonas¹, in preparing glass to metal seals, used fluxes to lower the softening point of the glass. In making seals by this method he states that, "The temperature interval through which the weld still cools after becoming solid then becomes shorter and the thermal stresses also become smaller." Zimmerman, Plankenhorn and Bennett² satisfactorily bonded a glazed K30 insulating brick to steel through the use of a low softening commercial ground coat enamel. Similar attempts by these authors were unsuccessful when a glass softening at a higher temperature was used.

c. Absorption of stresses by yielding. Another means by which cooling stresses can be reduced in metal-glass-ceramic bonds is through yielding or accommodation of one of the parts of the structure. Partridge³ cites the joining of copper to a wide range of glasses as an example of a low strength, ductile metal which yields during cooling of the seal, thus permitting relief of stresses developed in the glass. Butt type joints between glass and metals of unmatched thermal expansion coefficients are sometimes accomplished by shaping the metal edge into a thin wedge which is then forced into the soft glass; upon cooling, a portion of the differential contraction between glass and metal is accommodated by bending of the thin metal section.

In joining widely mismatched glasses and metals it is customary to employ a graded expansion joint in which several glasses of intermediate thermal expansion characteristics are used. The differential thermal contraction between the parts is then proportioned among the various glasses which make up the joint. By varying the number of glasses and the depth of each intermediate glass zone it is possible to distribute the stresses throughout the bonding zone rather than having them concentrated at the interface between the two component parts. It is interesting to note that in tubular joints between silica glass ($\alpha = 0.5 \times 10^{-6}$) and L1 sealing glass ($= 9.1 \times 10^{-6}$) as many as six intermediate glasses are used over a distance equivalent to three diameters of the tubing.

Absorption of a portion of the strain produced in cooling an unmatched metal-glass-ceramic joint is possible also by accommodation within the ceramic material itself. Since the modulus of elasticity is generally lower for a highly porous body it should yield more readily than a dense body and thus reduce stress concentrations. Partial compressive failure within the body might also permit further yielding.

d. Annealing of the glass bonding zone. The most advantageous temperature from which to rapidly cool a glass seal is that temperature at which the thermal expansions are most nearly the same for the component parts in an unstressed condition, providing also that no further viscous flow occurs

during cooling. Annealing at a temperature appropriate to the glasses being used serves to remove stresses by viscous flow within the glass. Upon further cooling to room temperature the seal is subject to only such strain as is produced by the differential thermal contraction within that limited temperature range. If the thermal expansion curves for the components of the seal separate most widely at some temperature between the annealing temperature and room temperature the strain in the seal would be greatest there and in such a case rapid, rather than slow cooling, would be most effective.

Annealing offers a further advantage where graded expansion joints are used. Since the glasses of lower thermal expansion generally have higher softening and annealing temperatures, it is possible to anneal each glass in the seal in its turn, thus reducing the overall contraction difference and, also, the stress magnitude.

2. Scope of the Investigation

The investigation was limited to development attempts to join ceramic materials to metal by means of a glassy bond. Although it was realized that high stresses would be produced in the joint because of the wide difference in thermal expansion of steel and the ceramic materials under consideration, previous work by these authors (see reference 2) had indicated that a certain amount of success might be expected. At the suggestion of representatives of the contracting authority the work was outlined to include the bonding to metal of thin square insulating ceramic tile of various sizes. It was expected to evaluate the insulating properties of 4 in. by 4 in. sheet metal specimens to which the various ceramic tile were thus fastened. This portion of the investigation was no longer appropriate when it became evident that the bonding of these ceramic tile could not be readily accomplished. The investigation then centered upon attempts to obtain a satisfactory metal-glass-ceramic joint using techniques and glass compositions which, on the basis of information available in the literature, offered the most promise for success.

III. EXPERIMENTAL DETAILS

1. Metal Preparation

Low carbon steel .052 in. thick was cut into blanks 2 in. by 4 in. and 4 in. by 4 in. These were scaled in an electric furnace for 3 minutes at 1400°F to burn off any grease or oil and were then sandblasted lightly to produce a clean rough surface to which the enamel coatings might readily adhere. The 2 in. by 4 in. blanks were used for those experiments in which the coatings were applied by dipping; the 4 in. by 4 in. blanks were coated by spraying.

2. Enamel Preparation

With the exception of coating No. 1104M-1, which was prepared from a commercially available frit, all enamels were prepared from raw materials by smelting, fritting, dry grinding of the frit and wet milling of the slip according to standard enamel preparation procedures. The compositions and measured thermal expansion coefficients of the frits are given in Table 1. The mill batch composition of the enamel coatings used are shown in Table 2. Thermal expansion curves were prepared from interferometer measurements for these frits and are reproduced in Figures 2 and 3. Bonding experiments were performed using coating No. 1104M-1 and two series of graded expansion coatings (Series A and Series B) as the bonding media (See Table 2). The soda-boro-silicate glasses were highly water soluble and extremely subject to aging effects. A second batch of these enamels was therefore prepared immediately prior to use in order to overcome this difficulty.

3. Body Preparation

An alumina porcelain, a zircon porcelain, and a cordierite body, the compositions, firing temperature and thermal expansion coefficients of which are listed in Table 3, were weighed in 2500 gram batches, dry mixed on a large sheet of paper and milled with 30 percent water content for 10,000 revolutions in a laboratory type porcelain ball mill. The resulting slips were poured in a thin layer over plaster of Paris bats such that the dried cake was approximately 3/16 in. thick. After each slip had partially dried it was cut into tile pieces either 1/4 in., 1/2 in. or 1 in. square. Upon further drying the pieces were easily removed. The zircon porcelain was fired to vitrification (0.0 porosity) at cone 12. The cordierite body slumped when fired at cone 1^{1/4}; tile pieces were therefore fired at cone 13 which resulted in a body porosity of 31 percent.

The alumina porcelain tile 1/2 in. and 1 in. square were fired to zero porosity by soaking for two hours at 2850°F in a gas fired Remmey kiln. These tile were set in A-10 alumina during firing. The 1/4 in. alumina porcelain tile, whose surfaces were in direct contact with each other, sintered together at this temperature requiring that another firing of these tile be accomplished at 2750°F. The latter firing produced 1/4 in. square alumina porcelain tile of approximately 35 percent porosity. This variation in porosity proved significant in later bonding experiments.

4. Application and Firing

Three groups of bonding experiments were investigated in each of which an unique glass bonding zone was studied, with exceptions to be noted later. The steel blanks of every

metal-glass-ceramic joint were first coated with 3 mils of coating No. 32-22 plus 3 mils of coating No. 110⁴M-1. Firing of the first coating at 1700°F. for six minutes served to form an adherent glass bond with the steel. The second coating, because of its low softening point, permitted the various metal and ceramic parts of the joint to contract independently of one another during cooling at temperatures above the strain point of this glass. This coating was fired at 1350°F for six minutes.

a. Coating No. 110⁴M-1

Coating No. 110⁴M-1 was used as a bonding glass between various ceramic tile and 2 in. by 4 in. steel specimens coated with base coat No. 32-22. Data regarding these experiments are given in Table 4. With exceptions as noted below, the specimens were prepared as previously described.

Tile pieces of the various bodies were placed in contact with the glassy coating of the metal specimen and fired for 15 minutes at 1350°F. and then cooled in air. Variations in coating thickness were accomplished by applying additional coating slip No. 110⁴M-1 over the prepared specimens and then imbedding the tile pieces in place. After drying, these composite metal-enamel-ceramic specimens were also fired for 15 minutes at 1350°F. One such specimen was also annealed for four hours at 850°F. and then allowed to cool with the furnace.

Additional methods of providing strain relief were attempted. In one case 15 mils of coating No. 110⁴M-1 were applied to the surface of a specimen previously coated with 3 mils of coating No. 32-22 and 20 mils of top coat No. 117-23. The ceramic tile were imbedded in this coating slip and fired at 1350°F for 15 minutes. It was thought that a portion of the strain produced by differential cooling might be accommodated by elastic deformation within the porous glass-bonded crystalline coating. In another instance, low carbon steel foil .002 in. thick was cleaned by scouring with enamel slip and 3 mils of No. 110⁴M-1 was applied by dipping, drying and firing for 6 minutes at 1350°F. Zircon porcelain and cordierite tile were placed in contact with this coated specimen and fired for 15 minutes at 1350°F. It was felt that, upon cooling, part of the differential contraction might be absorbed by elastic yielding of the thin highly stressed foil.

b. Series A Graded Expansion Coatings

A series of soda-boro-silicate glasses, the coefficients of linear thermal expansion in which varied from 12.1×10^{-6} to 4.0×10^{-6} cm/cm°C (100-500°) were prepared from compositions listed by Morey⁴. The fritted glasses were wet milled to form conventional enamel slips with 7 percent clay as

a suspending agent. These enamels were applied to low carbon sheet steel blanks in decreasing order of thermal expansion over 3 mils each of base coat No. 32-22 and No. 110⁴M-1. Thus a metal glass composite was prepared in which the thermal expansion varied from that of the metal to near that of the cordierite body (see Figure 2).

Two methods of application of these coatings were investigated. They were applied in 3 mil laminations by dipping, brushing off the reverse side of the coated specimen and firing each coating before the application of the next; and by spraying successive laminations of all series A coatings on the metal sample prior to firing. Each firing operation was conducted for six minutes at 1600°F in a box type electric furnace. An alumina porcelain, a zircon porcelain and a cordierite body prepared as tile pieces 1/8 in. thick and either 1/4 in., 1/2 in. or 1 in. square were fired under the above conditions in contact with the glassy surface of the enamel coated steel specimens. These bonding experiments included a comparison of the effects of annealing and cooling in air. Those samples cooled in air were fired in a manner similar to the firing of conventional enamels in that the composite metal-glass-ceramic joint was removed from the furnace and allowed to cool in air at room temperature. The samples which were annealed were removed from the furnace at the end of their firing cycle and immediately placed in another furnace held at 1200°F. These samples were annealed stepwise according to the following schedule in order to cover a wider range of annealing temperatures and to permit successive relief of strain in each of the laminated glassy coatings.

Annealing Schedule

<u>Time-Hours</u>	<u>Temperature - °F</u>
4	1200
16 (overnight)	1150
4	1100
4	1050
16 (overnight)	1000
4	950
4	900
16 (overnight)	850

Samples cooled in furnace to room temperature.

Data regarding these experiments are given in Table 5.

c. Series B Graded Expansion Coatings

Seven graded expansion coatings ranging from 10.5×10^{-6} to 5.0×10^{-6} cm/cm °C in measured coefficients of linear thermal expansion (100-500°C) were prepared from various commercial compositions listed by Partridge³. These coatings

were prepared and applied essentially as described above. The results of bonding experiments involving this series of coatings are given in Table 6.

IV. DISCUSSION OF RESULTS

The results of experiments in the bonding of ceramics to metal are given in Tables 4 through 6. The results for each of the bonding media are discussed separately in the following paragraphs.

1. 110⁴M-1 Coating (See Table 4)

The 1/4 in. square alumina porcelain, zircon porcelain and cordierite tile pieces did not adhere satisfactorily under conditions in which coating No. 110⁴M-1 was used alone as the bonding zone on .052 in. thick steel 2 in. by 4 in. coupons initially coated with base coat No. 32-22. With increased bonding zone thickness, the porous cordierite bodies showed some tendency to remain bonded but were easily removed by hand, leaving a portion of the body attached to the enameled surface. Annealing of specimens in which the ceramic tile were deeply imbedded in 80-90 mils of coating No. 110⁴M-1 did not prevent spalling of the cordierite and zircon porcelain tile; the alumina tile, possibly because of their higher thermal expansion, did not spall off but showed evidence of severe stress cracking in the surrounding bonding glass.

In applying coating No. 110⁴M-1 over a metal specimen previously coated with 20 mils of a porous crystalline top coat, some improvement was noted in the bond formed between this composite specimen and the porous cordierite body. Portions of the cordierite tile adhered to the specimen but were easily removed by hand. Failure of the cordierite tile occurred by internal shear failure of the tile itself. The alumina and zircon porcelain tile spalled off on cooling, but failure occurred within the bonding glass; a thin sheet of glass remained attached to the tile surface.

Cordierite and zircon porcelain tile pieces 1/2 in. and 1/4 in. square were bonded to carbon steel foil .002 in. thick with coating No. 110⁴M-1. A few zircon porcelain tile and practically all the cordierite bodies remained adherent. Although the metal foil undoubtedly yielded somewhat to relieve a portion of the thermal strain, the bonding zone remained under considerable stress; this was evidenced by some shear failure within the tile pieces. Most of the zircon porcelain tile spalled off completely but only partial shear failure occurred within the porous cordierite bodies.

It appeared from the above observations that a glass of low softening point could not be used alone to form a metal-ceramic bond between the components under consideration. Such a glass has been used however in bonding highly porous ceramic bodies of intermediate thermal expansion.

2. Series A Graded Expansion Coatings (See Table 5)

Shear failure within the glass bond occurred for all dense 1 in. and 1/2 in. square alumina porcelain tile regardless of the method of application of the glass zone, its thickness or its cooling treatment. Annealing, as previously described, materially improved the bonding of the 1/4 in. square alumina tile. Only one of these tile pieces adhered to specimen No. 8 which was cooled in air; however, all the 1/4 in. square alumina porcelain tile adhered satisfactorily to specimen No. 12 which was annealed. It should be noted that the failure of these porous 1/4 in. tile of the former specimen occurred through the tile themselves.

The zircon porcelain tile reacted extensively with the glass but spalled off during cooling. Shear failure occurred through the bonding glass down to the bare metal. There were minor indications of failure within the zircon porcelain tile; portions of the tile remained attached to the glass surface of the coated steel specimen. Using this series of bonding glasses, no permanent metal-zircon porcelain joints were obtained.

Cordierite bodies adhered to a metal specimen spray coated with this series of graded expansion glasses and annealed as previously described. The glass bonding zone was highly stressed as evidenced by the formation of stress cracks originating at the tile edges. Shear failures occurred both within the glass and within the cordierite tile.

The soda-boro-silicate glasses of this series which were spray coated and fired only once, possessed a coarse bubble structure. The glass bond thus prepared was undoubtedly of lower strength than either the same series of glasses when applied by dipping and firing successive coatings or the Series "B" graded expansion glasses.

3. Series B Graded Expansion Coatings (See Table 6)

The results of bonding experiments using this series of graded expansion commercial sealing glasses were only slightly more successful than those in which the soda-boro-silicate graded expansion glasses were used.

Annealing treatment improved the adherence of porous 1/4 in. square alumina tile applied over approximately 30 mils of the graded expansion coatings; however, a few tile of this type adhered satisfactorily when the specimen was cooled in air rather than annealed. Thicker application of the same coatings resulted in severe spalling of the glass bonding zone during cooling in air.

All of the 1 in. and 1/2 in. square zircon porcelain tile spalled readily from the 30 mil annealed coating; approximately one-half of the 1/4 in. square tile were very firmly bonded to the metal. For coating applications approximately 100 mils thick, annealing treatment resulted in the firm bonding of all the square zircon porcelain bodies except those 1 in. square.

All cordierite tile spalled from the 30 mil coatings regardless of cooling treatment, but all adhered very well to the 100 mil annealed graded expansion coatings.

With the exception of the porous alumina bodies of relatively high thermal expansion, every instance of successful bonding described above was associated with a convex curvature of the metal specimen indicating high stress levels.

V. SUMMARY

A limited investigation of the bonding of refractory ceramic materials to metal through the use of modified enameling techniques was undertaken. It was desired to determine the possibility of applying refractory thermal insulating ceramic bodies to extensive areas of sheet metal exhaust components for the purpose of reducing heat transfer. The results of this investigation indicate that a glass bond can be developed between steel and various ceramic bodies; however, this bond is generally subject to high stresses due to differential thermal contraction of the component metal and ceramic parts.

The limited success met with in these experiments did not permit a full qualitative evaluation of the effect of the variables under consideration. The difference in the thermal expansion of the bodies, for example, did not appear to be of major significance since it was possible to join all the ceramic materials to steel using bonding glasses. The difference in tile size seemed to influence the development of a satisfactory joint. Especially in the cases of the zircon porcelain and the cordierite bodies the smaller tile sizes seemed to be more resistant to failure by shearing of the bonding glass or of the body itself.

Of most significant interest is the success achieved with the porous 1/4 in. square alumina porcelain and the porous cordierite body. The high porosity of these bodies (35 and 31 percent respectively) may have been responsible for successful bonding in one or more of three ways. (1) The greater porosity may have permitted a wider zone of reaction between glass and ceramic thereby reducing stress gradients. (2) The lowered modulus of elasticity of the porous body may have permitted greater strain within the body thus reducing shear forces. (3) The low strength of these bodies may have permitted partial failure of the body by crushing thus relieving stresses caused by differential contraction.

The use of laminated glassy coatings, the coefficients of expansion of which varied from that of the metal to near that of the ceramic materials used, represented an attempt to absorb the differential thermal contraction over a greater distance between metal and ceramic. It is somewhat doubtful that these coatings retained their proper thermal expansion when fired in 3 mil increments. The convex nature of specimens coated with similar laminated coatings of greater thickness indicates that the individual thermal expansion characteristics were retained. Cordierite and zircon porcelain bodies bonded fairly readily to these coatings of greatest thickness. However, the additional weight of a thick graded expansion glass zone might not be warranted in certain applications of this bonding technique.

The results of this experiment seem to indicate that the greatest possibilities for utilization of this method of bonding are associated with the use of thin glass bonding zones and porous ceramic materials.

A need is felt for the quantitative analysis of stresses within the intermediate glass zone which bonds metal to ceramic, and also of the effects of the thermal expansion of the parts, the thickness of the glass and the annealing treatment of the seal upon these stresses.

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Table 1
Compositions⁽¹⁾ and Measured Thermal Expansion
Coefficients of Frits

Series A Bonding Glasses

Raw Batch Compositions

Frit No.	32	443	444	445	446	447	448
Quartz	34.25	40.4	36.0	65.4	56.2	46.4	58.1
Potash Feldspar	34.80	-	-	-	-	-	-
Borax	23.80	35.2	48.1	10.9	28.0	49.0	22.1
Boric Acid	-	-	-	-	-	-	19.7
Soda Ash	6.44	24.3	15.8	23.6	15.7	4.5	-
Soda Nitre	4.13	-	-	-	-	-	-
Alumina (A-10)	-	0.1	0.1	0.1	0.1	0.1	0.1
Fluorspar	3.71	-	-	-	-	-	-
Cobalt Oxide (Co ₃ O ₄)	0.50	-	-	-	-	-	-
Nickel Oxide (NiO)	0.50	-	-	-	-	-	-
Manganese Dioxide	1.50	-	-	-	-	-	-
Total	99.63	100	100	100	100	100	100

Oxide Compositions

SiO ₂	56.5	55.15	51.00	76.99	70.05	61.94	71.77
Al ₂ O ₃	8.38	0.21	0.20	0.19	0.16	0.20	0.15
B ₂ O ₃	10.55	17.60	24.86	4.68	12.79	23.92	23.78
Na ₂ O	12.06	27.25	24.14	18.33	17.16	14.14	4.45
K ₂ O	5.15	-	-	-	-	-	-
CaF ₂	4.48	-	-	-	-	-	-
CoO	0.56	-	-	-	-	-	-
NiO	0.60	-	-	-	-	-	-
MnO ₂	1.81	-	-	-	-	-	-
Total	100.09						

Coefficient of Linear
Thermal Expansion

$\frac{\text{cm}}{\text{cm } ^\circ\text{C}}$ (100-500°C) $\times 10^6$ 12.1 11.4 10.5 9.3 8.4 4.0

Table 1 (Continued)

Compositions⁽¹⁾ and Measured Thermal Expansion Coefficients of Frits

Series B Bonding Glasses

Raw Batch Compositions

Frit No.	GEC L2	BTH C12	449	BTH C40	GEC HH	450	Chance GS1
Quartz	52.9	44.1	50.8	52.8	60.3	61.0	59.2
Borax	-	18.4	17.8	18.7	18.0	29.7	24.4
Boric Acid	-	28.0	24.5	22.1	7.6	-	3.0
Soda Ash	8.2	-	-	-	-	0.2	-
Pearl Ash	9.9	8.5	5.7	5.0	4.9	-	-
Whiting	-	-	-	-	-	5.3	7.1
Magnesium Carbonate	-	-	-	-	5.3	-	-
Barium Carbonate	-	-	-	-	0.5	0.5	3.1
Lead Oxide	28.1	-	-	-	-	-	-
Alumina (A-10)	0.9	1.0	1.2	1.4	3.4	3.3	3.2
Total	100	100	100	100	100	100	100

Oxide Compositions

SiO ₂	56.5	57.4	64.8	65.9	72.0	73.0	74.5
Al ₂ O ₃	1.0	1.3	1.5	1.8	4.0	4.0	4.0
B ₂ O ₃	-	29.3	26.0	24.0	13.0	13.0	13.3
Na ₂ O	5.1	3.9	3.7	3.8	3.5	6.0	5.0
K ₂ O	7.2	7.6	5.0	4.2	4.0	-	-
CaO	-	-	-	-	-	3.5	5.0
BaO	-	-	-	-	0.5	0.5	3.0
MgO	-	-	-	-	3.0	-	-
PbO	30.0	-	-	-	-	-	-

Coefficient of Linear Thermal Expansion

$\frac{\text{cm}}{\text{cm } ^\circ\text{C}}$ (100-500°C) $\times 10^6$ 10.5 8.0 7.2 6.7 5.3 5.0

(1) Composition No. 1104M produced by the Chicago Vitreous Enamel Product Co. was also used in this investigation.

Table 2

<u>Enamel Mill Batch Compositions</u>								
<u>Coating No.</u>	<u>32-22</u>	<u>1104M-1</u>	<u>443-1*</u>	<u>444-1*</u>	<u>445-1*</u>	<u>446-1*</u>	<u>447-1*</u>	<u>448-1</u>
Frit(1)	88	100	100	100	100	100	100	100
Diaspore(2)	12	-	-	-	-	-	-	-
X-Brand Clay	7	7	7	7	7	7	7	7
Borax	0.75	0.75	-	-	-	-	-	-
Water	50	50	50	50	50	50	50	50

<u>Coating No.</u>	<u>GEC**</u> <u>L2</u>	<u>BTH**</u> <u>C12</u>	<u>449-1**</u>	<u>BTH**</u> <u>C40</u>	<u>GEC**</u> <u>HH</u>	<u>450-1**</u>	<u>Chance**</u> <u>GS1</u>
Frit(1)	100	100	100	100	100	100	100
X-Brand Clay	7	7	7	7	7	7	7
Borax	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Water	50	50	50	50	50	50	50

(1) The frit is designated by that portion of the coating number preceding the dash. All frits were preground to pass a 40 mesh sieve.

(2) First grade diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) preground to pass a 20 mesh sieve.

* Enamels of Series A

** Enamels of Series B

Note: All enamels were wet milled to a fineness of 2-4 gram dry residue on a 200 mesh sieve from a 100 gram sample.

Table 3

Body Properties

(Compositions, Firing Temperatures,
Porosities and Thermal Expansion
Coefficients)

<u>Body</u>	<u>Alumina Porcelain</u>	<u>Zircon Porcelain</u>	<u>Cordierite</u>
<u>Raw Materials</u>			
Alumina (A-10)	85	-	20
Zircon	-	59.25	-
Talc (Higrade sierramic)	2	-	40
Spodumene	-	-	10
Eryrite	5	-	-
Fluorspar	1	-	-
Whiting	2	-	-
Barium Zirconium Silicate	-	7.41	-
Magnesium Zirconium Silicate	-	7.41	-
Calcium Zirconium Silicate	-	7.41	-
Ball Clay	5	18.52	30
Firing Temp.	2 hrs. at 2850°F	Cone 12	Cone 13
Porosity (%)	0.0	0.0	31
Coefficient of Linear Thermal Expansion $\frac{\text{cm}}{\text{cm} \times ^\circ\text{C}}$ $\times 10^6$	7.3	4.2	2.8
(100-500°C)			

Table 4

Results of Experiments Utilizing Coating 1104M-1 (fired for fifteen minutes at 1350°F) as a Glass Bond Joining Tile Pieces of a Cordierite Body, a High Alumina Porcelain and a Zircon Porcelain with Base Coated Low Carbon Steel.

Specimen No.	Method of Coating Application	Coating Thickness (Mils)	Square tile Used (1/8" Thick)	Cooling Conditions	Remarks
1	Dipped on two sides	6-8	1 1/4" Z.P., Al ₂ O ₃ , Cord.	Air Cooled	Tile spalled off in large sheet; failure occurred through bonding glass; some zircon porcelain fragments adhering to glass
2	Coating slip poured on metal specimen	40-45	1/4" Z.P., Al ₂ O ₃ , Cord.	Air Cooled	All zircon porcelain, alumina porcelain and part of cordierite tile spalled off through bonding glass; some cordierite tile held in place but only weakly adherent.
3	Coating slip poured on metal specimen	80-90	1/4" Z.P., Al ₂ O ₃ , Cord.	Annealed 850°F 4 hrs. Furnace cooled	All tile except alumina porcelain spalled off; stress cracks evident near these tile.
4	Coating applied as mortar over 20 mils fired top coat No. 117-23	35	1/4", 1/2" Z.P.	Air Cooled	The zircon porcelain tile spalled off; failure occurred within the bonding glass.
5	Coating applied as mortar over 20 mils fired top coat No. 117-23	35-40	1/4" Al ₂ O ₃	Air Cooled	The alumina tile spalled off; failure occurred within the bonding glass
6	Coating applied as mortar over 20 mils fired top coat No. 117-23	35	1", 1 1/2", 1 1/4" Cordierite	Air Cooled	Approximately 30% of tile remained weakly adherent; failure of the tile occurred as shear failure through the tile itself and by failure of the crystalline top coat.

Table 4 - (continued)

Specimen No.	Method of Coating Application	Coating Thickness	Square Tile Used (1/8" Thick)	Cooling Conditions	Remarks
7	Coating 1104M-1 applied directly on .002" thick carbon steel foil	3-4	$\frac{1}{2}$ ", $\frac{1}{4}$ ", Z.P. Cord.	Air Cooled	Some failure of zircon porcelain by spalling of the enamel from the metal (failure at the metal-enamel interface); some shear failure within the zircon porcelain body. Cor-dierite tile adhered but showed visible signs of shear failure within the body; cracks in the tile were parallel to the enamel-ceramic interface.

Table 5

Results of Experiments Utilizing Series A Graded Expansion Coatings (Fired for six minutes at 1600°F) as a Glass Bond Joining Tile Pieces of a Cordierite Body, a High Alumina Porcelain and a Zircon Porcelain With Base Coated Low Carbon Steel.

Specimen No.	Method of Coating Application (to one side only)	Coating Thickness (Mils)	Square Tile Used (1/8" Thick)	Cooling Conditions	Cooling	Remarks
8	Dipping	25	1", $\frac{1}{2}$ ", $\frac{1}{4}$ ", $\frac{1}{8}$ " Al ₂ O ₃	Cooled in Air	All tile spalled off; failure of 1" and $\frac{1}{2}$ " tile occurred through glass bond in top glass layer; failure of $1\frac{1}{4}$ " (35% porosity) tile occurred through glass layer and by shear failure within the tile.	
9	Dipping	25	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Z.P.	Cooled in Air	All tile spalled off; failure through glass bond and by shearing of zircon porcelain tile pieces; particles of tile remain attached to glass surface.	
10	Dipping	25	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Cord.	Cooled in Air	All tile spalled off; failure through bonding glass; at ceramic-glass interface and by shear failure of tile.	
11	Spraying	65	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Al ₂ O ₃	Cooled in Air	Extensive shear failure throughout glass bonding zone for all tile.	
12	Dipping	25	$\frac{1}{2}$ ", $\frac{1}{4}$ ", 1" Al ₂ O ₃	Annealed	Shear failure in bonding zone between metal and 1" and $\frac{1}{2}$ " (zero porosity) tile; $\frac{1}{4}$ " (35% porosity) tile tightly adherent with occasional shear failure through tile body near ceramic-glass interface	

Table 5 (continued)

Specimen No.	Method of Coating Application (to one side only)	Coating Thickness (Mils)	Square Tile Used (1/8" Thick)	Cooling Conditions	Remarks
13	Dipping	25	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Z.P.	Annealed	All tile spalled off; shear failure in glass and tile.
14	Dipping	25	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Cord.	Annealed	All tile spalled off; failure occurred in bonding glass and as shear failure through tile pieces.
15	Spraying	65	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Al ₂ O ₃	Annealed	Extensive shear failure in glass bonding zone; tile adherent to top glass layer; numerous stress cracks originating in glass surface at edges of tile.
16	Spraying	65	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Z.P.	Annealed	Shear failure in glass bonding zone not so extensive as specimen No. 15; no adherent tile pieces.
17	Spraying	65	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Cord.	Annealed	Few adherent tile $\frac{1}{2}$ " and $\frac{1}{2}$ " square; some adherence of 1" tile which spalled off by shear failure through the tile itself.

Table 6

Results of Experiments Utilizing Series B Graded Expansion Coatings (Fired for Six Minutes at 1600°F) as a Glass Bond Joining Tile Pieces of a Cordierite Body, a High Alumina Porcelain and a Zircon Porcelain with Base Coated Low Carbon Steel.

Specimen No.	Method of Coating Application (to one side only)	Coating Thickness (Mils)	Square Tile Used (1/8" Thick)	Cooling Conditions	Remarks
18	Dipping	30	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Al ₂ O ₃	Cooled in Air	A few $\frac{1}{4}$ " porous tile adhered; all other tile spalled off by failure in glass.
19	Dipping	30	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Z.P.	Cooled in Air	All tile spalled; failure in glass.
20	Dipping	30	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Cord.	Cooled in Air	All tile spalled; failure in glass.
21	Spraying	100-110	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Al ₂ O ₃ , Z. P., Cord.	Cooled in Air	$\frac{1}{4}$ " alumina tile, $\frac{1}{4}$ " and $\frac{1}{2}$ " zircon porcelain tile well bonded, extensive shear failure in bonding glass caused spalling of all other tile.
22	Dipping	30	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Al ₂ O ₃	Annealed	90% of porous $\frac{1}{4}$ " alumina tile adhered; non-porous $\frac{1}{4}$ " and 1" tile spalled by shear failure in the glass.
23	Dipping	30	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Z.P.	Annealed	50% of $\frac{1}{4}$ " zircon porcelain tile adhered; failure of the tile pieces occurred by shearing of the glass bond and of the tile themselves.
24	Dipping	30	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Cord.	Annealed	No tile adhered; failure generally occurred within the tile with portions of the ceramic body remaining on the glass surface.

Table 6 (Continued)

Specimen No.	Method of Coating Application (to one side only)	Coating Thickness (Mils)	Square Tile Used (1/8" Thick)	Cooling Conditions	Remarks
25	Spraying	100-110	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Al ₂ O ₃	Annealed	Extensive shear failure within glass bonding zone; no tile adhered, shrinkage cracks on coating surface.
26	Spraying	100-110	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Z. P.	Annealed	1" tile pieces spalled off at glass ceramic interface; 50% of $\frac{1}{4}$ " and 50% of $\frac{1}{2}$ " tile pieces well bonded without the formation of visible surface stress cracks; remaining tile spalled off due to shear failure in glass bonding zone; specimen had slight convex curvature.
22	Spraying	100-110	$\frac{1}{4}$ ", $\frac{1}{2}$ ", 1" Cord.	Annealed	Two 1" tile pieces adhered; all of $\frac{1}{4}$ " and $\frac{1}{2}$ " pieces adhered; minor spalling within glass bond at specimen edges did not interfere with adherence of tile; specimen had highly convex curvature.

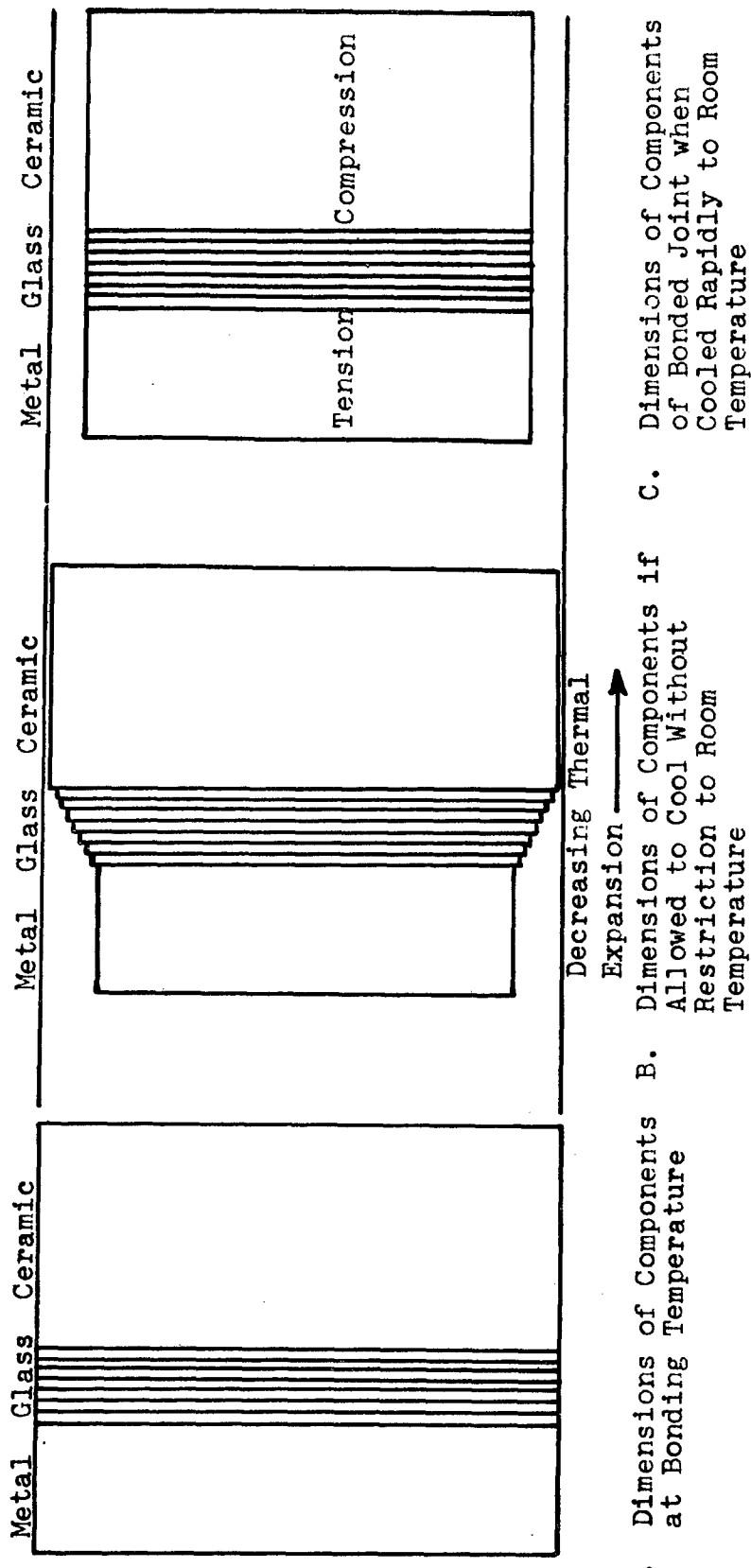


Fig. 1. Suggested thermal contraction diagrams of a hypothetical metal-glass-ceramic joint. The stresses are affected by the thickness, thermal contraction and modulus of elasticity of the metal, glass and ceramic.

